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14. ABSTRACT The goals of our research under AFOSR Grant number F49620-99-0191 (continued under F49620-02-0260) were to explore the preparation, properties and applications of organic matrix resin nanocomposites. The dispersed nanophases selected for this work included: (1) Polyhedral oligomeric silsesquioxane chemicals (POSS macromers) of three types: those with no polymerizable group, those with one reactive function and those with eight reactive functions. At first this included only the T8-POSS family (R <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> ), but later we expanded the work to the T10-POSS (R <sub>10</sub> Si <sub>10</sub> O <sub>15</sub> ) and T12-POSS (R <sub>12</sub> Si <sub>12</sub> O <sub>18</sub> ) families. (2) Vapor grown carbon nanofibers produced by ASI Cederville, OH (60-250 nm diameters). (3) Nanodispersed montmorillonite clays.				
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**FINAL REPORT ON AFOSR EPSCoR GRANT**  
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## Introduction

The goals of our research under AFOSR Grant number F49620-99-0191 (continued under F49620-02-0260) were to explore the preparation, properties and applications of organic matrix resin nanocomposites. The dispersed nanophases selected for this work included:

- (1) Polyhedral oligomeric silsesquioxane chemicals (POSS macromers) of three types: those with no polymerizable group, those with one reactive function and those with eight reactive functions. At first this included only the T<sub>8</sub>-POSS family (R<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>), but later we expanded the work to the T<sub>10</sub>-POSS (R<sub>10</sub>Si<sub>10</sub>O<sub>15</sub>) and T<sub>12</sub>-POSS (R<sub>12</sub>Si<sub>12</sub>O<sub>18</sub>) families.
- (2) Vapor grown carbon nanofibers produced by ASI Cederville, OH (60-250 nm diameters).
- (3) Nanodispersed montmorillonite clays.

In addition to studying each of these types of nanophases, studies were also carried out on adding two nanophases simultaneously to the resin matrices. Finally, we also studied C<sub>60</sub>/organic matrix nanocomposites and their response to laser irradiation.

Most of our work was carried out with thermoset resins to form crosslinked matrix nanocomposites because little work, prior to the beginning of our studies, had focused on either POSS chemicals or vapor grown carbon nanofibers within thermoset systems. Thermoset resins studied in this work included phenolics, cyanate esters, vinyl esters, dicyclopentadiene, styrene-divinylbenzene, crosslinked methyl methacrylate resins and epoxies. A limited amount of work was performed on thermoplastics.

During this work some of the **application highlights** that emerged included the items listed below.

1. We developed novel phenolic resin/carbon nanofiber composites with enormous high temperature erosion resistance, exhibiting potential for rocket nozzle or high temperature heat shield applications.
2. Carbon nanofiber organic matrix polymer rocket liner materials were developed in cooperation with the Edwards AFL at Edwards AFB, CA. Pittman was the lead author on an Air Force patent application which has now been filed on that work which claims the ability to shield motor casings with a thinner and lighter liner, allowing the use of more propellant (longer range on high payload). "Rocket Motor Insulations," C. U. Pittman, Jr., R. L. Blanski, S. H. Phillips, J. H. Koo and P. N. Ruth, Air Force Invention No AFB00685, *US Patent Application*, initiated Sept. 2, 2005, by the US Air Force.
3. Phenolic/POSS, phenolic/nanoclay, phenolic/carbon nanofiber, cyanate ester/POSS, cyanate ester/nanoclays and cyanate ester/carbon nanofiber composites pioneered in our lab are now being further investigated in a Phase I and Phase II STTR contract. They are being used as starting materials to prepare carbon-carbon composites with higher oxidation resistance and longer lifetimes in the 650-750 °C use range.

4. Our work on blending nanoparticles into phenolics which cure at low temperatures has attracted some initial Navy interest through Northrup Grumman (Ocean Springs, MS).
5. We have demonstrated the principle of using vapor grown carbon nanofiber/thermoplastic nanocomposites as organic vapor sensors with much greater reproducibility and lifetimes than current sensors using carbon black.

Some of the **major scientific highlights** of our work on the AFOSR grant include these items.

1. We developed a reproducible synthesis of both dodecaaminophenyl-T<sub>12</sub>-POSS and octaaminophenyl-T<sub>8</sub>-POSS.
2. Over the course of this work, we have developed a greater understanding of various mechanisms by which POSS derivatives may aggregate and phase separate into particle domains during resin crosslinking. In cases where POSS molecules can incorporate into the resin's chemical structure, the competing chemical incorporation kinetics versus phase separation kinetics as a function of structure have been examined in broader detail in our laboratory than anywhere else to date.
3. The most thorough and complete study of clay nanodispersion was recently published in *Macromolecules*. Small angle neutron scattering (SANS) was coupled with extensive high resolution TEM studies to define the tactoid size distributions (number of platelets per tactoid) along with d-spacing distributions in those tactoids. This work helped to clarify the mechanism by which clay exfoliation and clay particle cleavage occurs during nanodispersion of organically modified clays.
4. A combination of molecular dynamics computations and ab-initio quantum mechanical calculations have helped elucidate the effects of POSS moieties on polymer properties and molecular motion. We also studied the structure, stability and electronic properties of endohedral complexes of POSS where the endohedral species are alkali metals, alkali cations, halides, noble gases and more recently transition metal atoms and ions.

### Polyhedral Oligomeric Silsesquioxane/Organic Matrix Nanocomposites

**Major reviews of POSS polymer and copolymer chemistry.** The first review was published in Sept. 2001<sup>1</sup> and updated in 2005.<sup>2</sup> This is now widely cited by those in the field. This review describes the synthesis and properties of homopolymers, copolymers and nanocomposites of monomers containing inorganic-organic hybrid polyhedral oligomeric silsesquioxane (POSS) structures. Monomers, such as styryl-POSS, methacrylate-POSS, norbornyl-POSS, vinyl-POSS, epoxy-POSS and siloxane-POSS, are included. Both monofunctional and multifunctional POSS macromers are included. Thermoplastic and thermoset systems are considered. Thermal, rheological and dynamic mechanical properties are described. The synthesis of POSS-macromers (monomers) is briefly described. POSS chemicals have been used to prepare nanosized designed novel composites with a variety of potential applications. The original version of the review, covering about 170 references, is descriptive and not designed to be totally comprehensive. However, the major existing reviews of certain subtopics are noted,

allowing the reader to gain a general introduction while providing the information to permit more comprehensive coverage.

A large amount of experimental work performed and subsequently published.

**The incorporation of both monofunctional and multifunctional polyhedral oligomeric silsesquioxane (POSS) derivatives into crosslinked resins.** Mono- and polyfunctional POSS monomers have been dissolved into resin monomers and cured as a route to synthesize hybrid organic/inorganic nanocomposites.<sup>3</sup> The central cores of POSS molecules contain an inorganic cage with  $(\text{SiO}_{1.5})_n$  stoichiometry where n=8,10 and 12. Each Si atom is capped with one H or R function giving an organic outer shell surrounding the nanometer-sized inorganic inner cage. By including polymerizable functions on the R groups, a hybrid organic/inorganic macromer is obtained which can be copolymerized with organic monomers to create thermoplastic or thermoset systems. We have focused on incorporating POSS derivatives into crosslinking resins of the following types: (1) dicyclopentadiene (2) epoxies (3) vinyl esters (4) styrene-DVB (5) MMA/1,4-butane dimethacrylate (6) phenolics and (7) cyanate esters.<sup>3</sup> One goal has been to determine if molecular dispersion of the POSS macromers has been achieved or if various degrees of aggregation occur during crosslinked resin formation. As network formation proceeds, a kinetic race between POSS molecular incorporation into the network versus phase separation into POSS-rich regions (which then polymerize) occurs. Ultimately, we have worked to determine the effects of such microstructural features on properties. Combustion of these hybrids creates a  $\text{SiO}_2$ -like surface layer that retards flame spread. Dynamic mechanical properties have been studied.

**POSS/vinyl ester composites.**<sup>4</sup> How would POSS chemicals disperse? How would potential chemical reactions occur versus phase separation?

Vinyl ester (VE) composites containing chemically bonded, multifunctional polyhedral oligomeric silsesquioxane (POSS), POSS-1,  $((\text{C}_6\text{H}_5\text{CHCHO})_4(\text{Si}_8\text{O}_{12})(\text{CH}=\text{CHC}_6\text{H}_5)_4)$  nanoparticles were prepared with VE/POSS-1 95/5 and 90/10 wt/wt ratios.<sup>4</sup> The mole percents of POSS-1 in these two composites are low (<0.5% and <1%, respectively) due to the high mass of POSS-1 (mwt=1305). VE composites of two nonfunctional POSS-3 (octaisobutyl POSS) and POSS-4 (dodecaphenyl POSS) derivatives were also prepared with 95/5 wt/wt compositions. Additionally, POSS-1 was also incorporated into styrene copolymers at levels of 5wt% (0.42mole%) and 10wt% (0.88mole%) of POSS-1. The composites and copolymers were characterized by dynamic mechanical thermal analysis (DMTA) and mechanical testing. The POSS-1 units incorporated into the vinyl ester network were well dispersed. No phase-separation in the VE/POSS-1 90/10 composite could be detected by TEM from low to  $8\times 10^5$  magnification.

In VE composite containing 10wt% POSS-1, silicon-rich phases were observed ranging in size from a few nm to ~75nm by electron energy loss spectroscopy (EELS).<sup>4</sup> TEM, EDXS, EELS and extraction studies suggest that some POSS-1-rich nanoparticles in the VE/POSS-1 90/10 composite are present and also a fraction of the POSS-1 is molecularly dispersed within the VE resin. The POSS-1-rich dispersed phase portion is crosslinked, insoluble and contains some VE. VE/POSS-3 and VE/POSS-4 composites exhibited larger-sized POSS phases which do not contain VE. Incorporating the low mole percentages of POSS-1 into the VE network by chemical bonds or blending

nonfunctional POSS-3 or 4 into VE resin has almost no influence on  $T_g$  or on the width of the  $\tan\delta$  peak in the glass transition range.<sup>4</sup>

POSS-1-styrene copolymers exhibit good miscibility at 5wt% POSS-1, but serious phase-separation occurs in the copolymer with 10wt% POSS-1 content.<sup>4</sup> POSS-1-styrene copolymers swelled but did not dissolve in THF demonstrating they had been crosslinked by POSS-1. No POSS-1 was extracted into the THF. The POSS-1-styrene copolymers have higher  $T_g$  values versus pure polystyrene (PS) prepared at the same conditions. The  $T_g$  elevation could be due to the crosslinking resulting from the four  $\beta$ -substituted styryl functions in POSS-1 and due to the effect of high molecular weight POSS units retarding segmental motion of a portion of the chain segments.<sup>4</sup> The  $T_g$  of the 10wt% POSS-1 copolymer is almost the same as that of the 5wt% POSS-1 copolymer because the continuous phase in the 10wt% POSS-1 copolymer might have a crosslinking density similar to that of the 5wt% POSS-1 copolymer. The low POSS-1 mole% means that many all-styrene segments exist that can undergo segmental motion with being retarded by POSS. The  $\tan\delta$  peak for 10wt% POSS-1 copolymer is much broader and less intense than that for PS or 5wt% POSS-1 copolymer. A higher average crosslinking density and much less segmental motion in the dispersed POSS-1-rich phase account for this behavior in the 10wt% copolymer.<sup>4</sup>

The bending storage modulus,  $E'$ , values of the VE/POSS-1 composites and the POSS-1-styrene copolymers are higher than those of either the neat vinyl ester resin or pure PS, respectively, over entire temperature range, especially at the low POSS-1 content (5wt%).<sup>4</sup> The incorporation of multifunctional POSS-1 into vinyl ester or PS by chemical bonding improves the thermal dimensional stabilities. The flexural modulus of the vinyl ester resin is raised by incorporation of POSS-1 while the flexural strengths are lowered.<sup>4</sup> VE resin and VE/POSS-1 composites gave negligible weight gain after 50 days in toluene. The VE and composite samples cracked and fragmented after submersion in THF.<sup>4</sup>

**Epoxy/POSS nanocomposites.** Epoxy/POSS systems were also carefully studied.<sup>5</sup> Aliphatic epoxy composites with multifunctional polyhedral oligomeric silsesquioxane (POSS) ( $(C_6H_5CHCHO)_4(Si_8O_{12})(CH=CHC_6H_5)_4$ ) nanophases (epoxy/POSS 95/5 and 75/25), and epoxy blends with the prepolymer of ladderlike polyphenylsilsesquioxane (PPSQ) (95/5, 90/10 and 85/15) were prepared by solution casting and then curing.<sup>5</sup> These composites and blends were studied by dynamic mechanical thermal analysis (DMTA) and mechanical testing. The POSS units incorporated into epoxy network are well dispersed in the composite, probably on the molecular scale, even at high POSS content (25wt%) based on TEM observations. However, the aliphatic epoxy / PPSQ blends exhibit good miscibility only at low PPSQ content ( $\leq 10$ wt%). Phase-separation was clearly observed when the PPSQ content was 15%. Incorporation of the POSS macromer into this epoxy network by curing at upper temperatures of 120 and 150 °C broadened the temperature range of glass transition of the resulting composites but has almost no influence on their  $T_g$  (the  $\tan\delta$  peak temperature). The  $T_g$  of epoxy/PPSQ blends containing  $\leq 10$ wt% PPSQ increased slightly with increasing PPSQ content. However, the  $T_g$  of epoxy/PPSQ 85/15 is lower than that of the neat epoxy resin because crosslinking density is reduced in the blend.

Inclusion of PPSQ into the epoxy resin has no effect on the width of their glass transition range.<sup>5</sup> The storage moduli  $E'$  of both epoxy/POSS composites and

epoxy/PPSQ blends at  $T > T_g$  are higher than those of neat epoxy resin and increase with the POSS or PPSQ content, improving their thermal dimensional stability. The flexural modulus of the epoxy resin is raised by POSS incorporation or PPSQ addition.<sup>5</sup> Modification of the epoxy resin's flexural modulus is larger for composites with molecularly dispersed POSS than for those containing PPSQ.<sup>5</sup> The magnitude of this increase goes up as more POSS or PPSQ was added. But, the flexural strengths of epoxy/POSS nanocomposites and epoxy/PPSQ blends are lower than that of neat epoxy.

**The synthesis, morphology and viscoelastic properties of cyanate ester/POSS nanocomposites.** A major study of cyanate ester/POSS nanocomposites was undertaken to provide the background understanding for eventual use of these composites to make carbon-carbon composites.<sup>6-8</sup>

Cyanate ester (PT-15, Lonza Corp) composites containing the inorganic-organic hybrid polyhedral oligomeric silsesquioxane (POSS), octaaminophenyl(T<sub>8</sub>)POSS, **1**, (C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>8</sub>(SiO<sub>1.5</sub>)<sub>8</sub> were synthesized.<sup>6</sup> These PT-15/POSS-**1** composites (99/1, 97/3 and 95/5 wt%/wt%) were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic mechanical thermal analysis (DMTA), solvent extraction and FT-IR. The T<sub>g</sub> values of the composite with 1wt% **1** increased sharply vs. the neat PT-15 but 3 and 5wt% of **1** in these cyanate ester composites depressed T<sub>g</sub>.<sup>6</sup> All PT-15/POSS composites exhibited higher E' values (at T > T<sub>g</sub>) than the parent resin, but these values decreased going from 1 to 5 wt% of POSS. Tanδ peak intensities decreased and their widths broadened upon incorporation of POSS. XRD, TEM and IR data are all consistent with molecular dispersion of **1** due to the chemical bonding of the octaamino POSS-**1** macromer into the continuous cyanate ester network phase. The amino groups of **1** react with cyanate ester functions at lower temperatures than where cyanate ester curing by cyclotrimerization occurs.

In contrast to **1**, 3-cyanopropylheptacyclopentyl(T<sub>8</sub>)POSS, (C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>(SiO<sub>1.5</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN, **2**, has a low solubility in PT-15 and does not react with the resin below or at the cure temperature.<sup>6</sup> Thus, phase separated aggregates of **2** are found in samples containing from 1 to 10wt% of **2**. Nevertheless, the T<sub>g</sub> and E' values (T > 285 °C) of these composites increase regularly with an increase in 2.6

Octaaminophenyl(T<sub>8</sub>)POSS [**1**, (C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>8</sub>(SiO<sub>1.5</sub>)<sub>8</sub>] and dodecaaminophenyl(T<sub>12</sub>)POSS [**2**, (C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>12</sub>(SiO<sub>1.5</sub>)<sub>12</sub>] were synthesized, characterized and then incorporated into two types of thermoset resins: (1) the bisphenol-F-based cyanate ester resin, PT-15, and (2) epoxy (Epon 828, Shell Chemical Corp.)/4,4'-diaminodiphenylmethane (DDM) resin, respectively, to make two series of nanocomposites.<sup>7</sup> The sum of amino groups in both DDM and POSS were held in a 1:1 mole ratio to the epoxy groups. EPON-828/1/DDM and EPON-828/2/DDM composites (78.63/0/21.37, 77.48/5/17.52, 76.34/10/13.66, 74.05/20/5.95 and 72.28/27.72/0 wt/wt/wt compositions for both series) were prepared.<sup>7</sup> PT-15/**1** and PT-15/**2** composites (99/1, 97/3 and 95/5 wt/wt compositions for both types) were also prepared. These nanocomposites were characterized by transmission electron microscopy (TEM), dynamic mechanical analysis (DMA), solvent extraction and FT-IR. In all systems, POSS **1** and **2** were chemically bound into the resin matrix and phase-separated POSS particle domains were not observed. Incorporation of both **1** and **2** can dramatically elevate the high temperature bending storage moduli, E', of epoxy resins.

Cyanate ester (PT-15, Lonza Corp) composites containing the blended polyhedral oligomeric silsesquioxane (POSS), TriSilanolPhenyl-POSS ( $C_{42}H_{38}O_{12}Si_7$ ), were prepared containing PT-15/POSS 99/1, 97/3, 95/5, 90/10 and 85/15 w/w ratios.<sup>8</sup> The composites were characterized by FT-TR, X-ray diffraction (XRD), small-angle neutron scattering (SANS), scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (X-EDS), transmission electron microscopy (TEM), dynamic mechanical thermal analysis (DMTA) and three-point bending flexural tests.<sup>8</sup> TriSilanolPhenyl-POSS was thoroughly dispersed into uncured liquid PT-15 resin. After curing, XRD, SANS and X-EDS measurements were consistent with partial molecular dispersion of a portion of the POSS units in the continuous matrix phase while the remainder forms POSS aggregates. Larger aggregates are formed at higher loadings.

SANS, SEM and TEM show that TrisilanolphenylPOSS-enriched nanoparticles are present in the PT-15/POSS composites.<sup>8</sup> The storage bending moduli,  $E'$ , and the glass transition temperatures,  $T_g$ , of PT-15/POSS 99/1, 97/3 and 95/5 composites are higher than those of the pure PT-15 over the temperature range from 35 – 350 °C.<sup>8</sup> The  $E'$  values for all these composites (except for the 15 wt% POSS sample) are significantly greater than that of the pure resin at  $T > T_g$ . Therefore, small amounts ( $\leq 5$  wt%) of TriSilanolPhenyl-POSS incorporated into cyanate ester resin PT-15 can improve the storage modulus and the high temperature properties of these cyanate ester composites versus the pure PT-15 resin. The flexural strength and flexural modulus is also raised by POSS incorporation.<sup>8</sup>

#### **Crosslinked methyl methacrylate resins with a mono-methacrylate functionalized heptaisobutyl POSS.<sup>9</sup>**

A mono-methacrylate POSS derivative was incorporated into crosslinked methyl methacrylate matrices.<sup>9</sup> The morphologies and properties were then studied. Poly(isobutyl methacrylate-co-butanediol dimethacrylate-co-3-methacrylylpropylheptaisobutyl( $T_8$ )polyhedral oligomeric silsesquioxane) (P(iBMA-co-BDMA-co-MA-POSS)) nanocomposites with different crosslink densities (BDMA loadings of 1, 3 and 5wt%) and different MA-POSS percentages (5, 10, 15, 20 and 30wt%) have been synthesized by radical-initiated terpolymerization.<sup>9</sup> Linear P(iBMA-co-MA-POSS) copolymers were also prepared.<sup>9</sup> Viscoelastic properties and morphologies were studied by DMTA, confocal microscopy and TEM. The viscoelastic properties depend on the crosslink density. The dependence of viscoelastic properties on MA-POSS content for the nanocomposites at low BDMA loading (1wt%) is similar to that of linear P(iBMA-co-MA-POSS) copolymers. P(iBMA-co-1wt%BDMA-co-10wt%MA-POSS) exhibits the highest  $E'$  values in the rubbery region of this series. The 30wt% MA-POSS nanocomposites with 1wt% BDMA exhibits lowest  $E'$  values. However, the  $E'$  values in the rubbery region for P(iBMA-co-3wt%BDMA-co-MA-POSS) nanocomposites with 15wt% and 30wt% MA-POSS are higher than those of the parent P(iBMA-co-3wt%BDMA) resin.<sup>9</sup> MA-POSS raises the  $E'$  values of all P(iBMA-co-5wt%BDMA-co-MA-POSS) nanocomposites in the rubbery region above those of P(iBMA-co-5wt%BDMA), but MA-POSS has little influence on  $T_g$  values at  $\leq 15$  wt% POSS and slightly reduces  $T_g$  values at 20 and 30wt% POSS. Heating history has a little influence on the viscoelastic properties. No POSS aggregates are observed for the P(iBMA-co-1wt%BDMA-co-MA-POSS) nanocomposites by TEM.<sup>9</sup> POSS-rich particles

with diameters of several microns are present in the nanocomposites with 3 and 5wt% BDMA.<sup>9</sup>

**Phenolic resin/POSS composites.** A variety of phenolic resins have been studied containing multifunctional or monofunctional and unfunctionalized POSS macromers in a manner similar to that described for cyanate esters.<sup>10</sup> A portion of this work is summarized below.

Three classes of inorganic-organic hybrid phenolic resin/polyhedral oligomeric silsesquioxane (POSS) nanocomposites were synthesized. Multifunctional dichloromethylsilylheptaisobutyl-POSS (POSS-1), trisilanolheptaphenyl-POSS (POSS-2), and poly(phenylsilsesquioxane) uncured POSS (POSS-3) were employed.<sup>10</sup> Nonfunctional POSS-4 (octaisobutyl-POSS) was blended into the uncured phenolic resin and cured under the same conditions used for the other three nanocomposite classes.<sup>10</sup> Weight ratios of 99/1, 97/3, 95/5 and 90/10 were prepared for the POSS-1, 2 and 4 series and 99/1, 97/3 and 95/5 ratios for the POSS-3 nanocomposites.<sup>10</sup> POSS-1 incorporation into this phenolic resin network increases T<sub>g</sub> and broadens the tanδ peak (DMTA) range. T<sub>g</sub> and E' values at T>T<sub>g</sub> both increase with higher POSS-1 content. In contrast, incorporating 5wt% of POSS-2 into the phenolic resin network lowers T<sub>g</sub> to 193 °C from 213 °C for the neat phenolic resin. All values of E' for POSS-2 composites were higher, than those of the phenolic control in both glassy and rubbery regions. The T<sub>g</sub> values of the 1 and 10% POSS-2 systems were higher. Incorporating 10wt% of POSS-1 or POSS-2 improved the heat distortion temperature and moduli (E' = 123 and 201GPa at 265 °C, respectively, versus 56GPa for the pure phenolic resin). Increases in E' for T>T<sub>g</sub> and T<T<sub>g</sub> were also observed for all POSS-3 nanocomposites. However, the E' at T>T<sub>g</sub> and the T<sub>g</sub> values of the POSS-4 composites were lower than those of the control resin. Octaisobutyl POSS-4 cannot form chemical bonds to the resin and could be extracted from its composites with THF. POSS derivatives were not present in residues extracted by THF from the phenolic resins containing POSS-1, 2 or 3, because each of these derivatives were chemically bound within the phenolic resin. Subsequent heating cycles produce much larger increases in T<sub>g</sub> and E' values in the rubbery region for the POSS-1, 2 and 3 composites than for the neat phenolic resin or for the POSS-4 systems.<sup>10</sup>

#### **Phase separation/nano domain formation in phenolic resin/POSS composites.**

Formation of nano POSS domains is currently an area under active study growing out of the last year of the AFOSR grant.<sup>11</sup> The structure and properties of organic-inorganic hybrid nanocomposites prepared from a resole phenolic resin and a POSS mixture containing >95 wt% trisilanolphenyl POSS was investigated by POM (polarized optical microscopy), SEM, TEM, WAXD, FT-IR, DSC and TGA techniques.<sup>11</sup> Composites with 1.0 - 10.4 wt% of POSS were prepared by dissolving the POSS and the phenolic resin into THF, followed by solvent removal and curing. Both nano- and micro-sized POSS filler aggregates and particles were shown to be heterogeneously dispersed in the cured matrix by POM, TEM, SEM and X-EDS. POSS was found everywhere, including in both dispersed phase domains and in the matrix. The nanocomposite morphology appears to form by a multi-step POSS aggregation during the process of phase separation.

Both the matrix and dispersed "particulate" phase domains are mixtures of phenolic resin and POSS.<sup>11</sup> POSS micro-crystals act as the core of the dispersed phase. The bigger dispersed domains consist of smaller particles or aggregates of POSS molecules that exhibit some order but regions of matrix resin are interspersed. A WAXD

peak at  $2\theta \sim 7.3^\circ$  indicates crystalline order in the POSS aggregates.<sup>11</sup> This characteristic peak's intensity increases with an increase in POSS loading, suggesting that more POSS molecules have aggregated or crystallized. FT-IR spectra confirm that hydrogen bonding exists between the phenolic resin and POSS Si-OH groups. This increases their mutual compatibility, but H-bonding does not prevent POSS aggregation and phase separation during curing. TGA measurements in air confirmed the temperature for 5% mass loss increases with increase of POSS loading and at  $T > 550^\circ$  the thermal stability increases more sharply with POSS loading.<sup>11</sup> The nanocomposite glass transition temperatures ( $T_g$ ) are only slightly affected by the POSS filler.<sup>11</sup>

### Rheological properties of poly(methyl methacrylate/rigid ladder-like polyphenylsilsesquioxane blends.

Polystyrene (PS) blends with rigid ladderlike polyphenylsilsesquioxane (PPSQ) were prepared by solution casting followed by hot pressing.<sup>12</sup> The rheological properties of these blends were studied under dynamic shear and uniaxial elongation conditions.<sup>12</sup> The loss modulus ( $G''$ ) and dynamic shear viscosity ( $\eta^*$ ) of the 95/5 PP–PPSQ blend were slightly lower than those of pure PS at low frequencies ( $\leq 10^{-2}$  rad/s). However, the storage modulus ( $G'$ ),  $G''$ , and  $\eta^*$  of the other blends (90/10, 85/15, and 80/20) were higher than those of pure PS and increased with PPSQ content. The  $\eta_E$  data demonstrated that PS–PPSQ blends exhibited slightly weaker (5% PPSQ) or much weaker (10% PPSQ) strain hardening than PS. In contrast, the 85/15 and 80/20 PP–PPSQ blends showed strain softening, and the extent of strain softening increased with PPSQ content. PS entanglements might have been reduced by the specific interactions between PS and PPSQ, which locally ordered some PS molecules in the 95/5 blend sample, because most of the PPSQ might have been well dispersed in the PS continuous phase, and only a few small PPSQ particles ( $\sim 1.3 \mu\text{m}$ ) were formed because of good miscibility. However, at high PPSQ contents ( $\geq 10\%$ ), many larger hard PPSQ particles were formed, which acted as fillers during the rheological measurements.<sup>12</sup>

**Computational chemistry studies of POSS complexes and POSS-containing polymers.**<sup>13,14</sup> Endohedral and exohedral polyhedral cage molecules of the form  $(\text{HAO}_{3/2})_8$  ( $\text{A} = \text{C, Si, Ge}$ ) with double four-membered ring D4R units complexed with the atomic or ionic species ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , He, Ne, Ar) have been investigated by **ab-initio-calculations** at the B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels.<sup>13</sup> Geometric, electronic, and energetic properties were obtained. For the endohedral complexes the noble gas atoms ( $\text{X} = \text{He, Ne and Ar}$ ) inside the cage cause the cages to expand, and the extent of the expansion depends on the size of the included atom. Endohedral alkali ions, in contrast, exhibit both attractive and repulsive interactions with the cage atoms. The cage expands when  $\text{X} = \text{K}^+$  and contracts when  $\text{X} = \text{Li}^+$  or  $\text{Na}^+$  for  $\text{A} = \text{Si, Ge}$ , and for  $\text{A} = \text{C}$ , the cage expands for all three ions.

Encapsulation of the halide ions by  $\text{T}_8\text{-POSS}$  results in cage expansion.<sup>13</sup> Furthermore, the symmetry of the endohedral complexes when  $\text{X}$  is a cation depends critically on the relative cation and cage sizes. The binding energies of the endohedral and exohedral complexes document a clear preference for the latter, except for halides, where the endohedral complexes are more stable. The stability of endohedral complexes containing the isoelectronic species  $\text{X} = \text{Na}^+$ , Ne, F<sup>-</sup> is determined by the charge transfer to the A-O cage bonding sites. The formation of the endohedral complexes is discussed

in terms of transition states that connect the exohedral and endohedral minima as well as the activation barriers for insertion of the guest into the cage.<sup>13</sup> Our studies predict that a fluoride anion can penetrate into the  $(\text{HAO}_{3/2})_8$  cage without destroying it. For  $\text{X} = \text{Cl}^-$ , in contrast, the cage ruptures upon insertion of the impurity.

More recently a large series of  $T_8$ -POSS,  $T_{10}$ -POSS and  $T_{12}$ -POSS endohedral complexes have been studied where the endohedral species are noble gases, halide ions, alkali metals, cations and anions and transition metal atoms and cations. This large body of work has been described in the PhD Dissertation of Delwar Hossain (Mississippi State University, 2006), but it has not yet been submitted for publication.

**Molecular dynamics simulations** were carried out on copolymers of both styrene and methyl methacrylate with polyhedral oligomeric silsesquioxane (POSS) derivatives to identify the origin of the property changes imparted upon the chemical incorporation of POSS.<sup>14</sup> Simulations were carried out on these hybrid copolymers and the parent homopolymers to elucidate the effect of the  $T_8$ ,  $T_{10}$ , and  $T_{12}$  POSS cages. These POSS comonomers were derivatized with a single polymerizable function and 7, 9 and 11 nonpolymerizable hydrocarbon moieties, respectively. Glass transition temperatures ( $T_g$ ) were computed from specific volume versus temperature plots.<sup>14</sup> The packing of POSS units around the polymer backbone was analyzed via their radial distribution functions. The effect of POSS on polymer motion was analyzed through the mean square displacement function. The improvements in the elastic moduli upon incorporation of POSS were computed by employing the static deformation method.<sup>14</sup>

#### **Fullerene-doped copolymers of methyl methacrylate. Laser Irradiation/Photoluminescence.**<sup>15,16</sup>

Photoluminescent materials based on laser-modified fullerene-doped polymer thin films were reviewed and experimental studies were performed.<sup>15,16</sup> Some fullerene-doped polymer films exhibit stronger photoluminescence (PL) than films of the pure fullerene or the pure polymer. Photoluminescence (PL) intensities of  $C_{60}$ -doped poly(methyl methacrylate-co-ethyl acrylate) (P(MMA-co-EA)) and poly(methyl methacrylate-co-methacrylic acid) (P(MMA-co-MAA)), increase gradually during laser irradiation in air.<sup>16</sup>  $C_{70}$ -doped copolymers exhibit a rapid increase in PL intensity soon after the start of laser irradiation, but the PL intensities then decrease to a minimum upon further irradiation. After that, their PL intensities increase again, similar to that of  $C_{60}$ -doped copolymers. By analyzing UV-visible spectra, these increases in PL are attributed to the formation of some fullerene oxide-copolymer complex by laser induced photochemical oxidation reactions.<sup>15,16</sup>

Especially, large PL increases have been observed from fullerene ( $C_{60}$  or  $C_{70}$ )-doped polymer thin films after laser irradiation in air for some time.<sup>15,16</sup> PL peaks for these materials are broadened with some blue-shifting after laser modification. These polymers include poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(isopropyl methacrylate) (PIPMA), poly(isobutyl methacrylate) (PiBMA), poly(methyl methacrylate-co-ethyl acrylate) (P(MMA-co-EA)), poly(methyl methacrylate-co-methacrylic acid) (P(MMA-co-MAA)), polystyrene (PS), poly(methyl phenyl silane) (PMPS) and poly(phenyl silsesquioxane) (PPSQ).<sup>15,16</sup>  $C_{60}$  or  $C_{70}$ -doped PE MA thin films have the greatest PL enhancements after laser irradiation modification in air among the polymer listed above.<sup>16</sup> Both the extent of PL increase and rate of PL growth depend on the polymer structure and the fullerene concentration. This great

increase in the magnitude of PL is caused by oxidized fullerene-polymer adducts formed during laser-induced photochemical reactions.

### Nanoclay Organic Matrix Resin Composites.<sup>17-20</sup>

Highly delaminated polydicyclopentadiene/clay nanocomposites were synthesized by *in situ* polymerization of dicyclopentadiene/organically-modified montmorillonite dispersions.<sup>17</sup> Dicyclopentadiene/clay suspensions were sonicated for various times to enhance the degree of delamination prior to curing.<sup>17</sup> The d-spacings of the clay in nanocomposites were monitored using X-ray diffraction and the extent of delamination was examined by TEM and preliminary neutron scattering studies. A new approach, use of confocal laser microscopy was employed to follow the dispersion of clay layers, tagged by a fluorescent dye, within the liquid monomer.<sup>17</sup> It is evident that XRD can not be used alone as a criteria for exfoliation. TEM showed that increasing the clay concentration at constant sonication gave an increase in average tactoid size. The largest improvement in composite mechanical properties occurred at clay loading levels (0.5-1wt%). Significant increases in T<sub>g</sub>, elastic bending moduli, flexural moduli and flexural strengths were found at 0.5-1wt% clay loadings, where the highest degree of delamination/exfoliation also occurred.<sup>17</sup>

Clay delamination in clay/poly(dicyclopentadiene) nanocomposites was quantified by a combination of small angle neutron scattering and high resolution transmission electron microscopy.<sup>18</sup>

Highly delaminated clay/poly(dicyclopentadiene) nanocomposites were prepared by *in-situ*, ring-opening metathesis polymerization of pre-sonicated mixtures of the liquid dicyclopentadiene (DCPD) and organically-modified Montmorillonite clays.<sup>18</sup> Three nanocomposite series (using Montmorillonites: I-28, I-44pa) of increasing clay loadings (0.5, 1.0, and 2.0 wt%) and modified Montmorillonite PGW (0.5wt%) were synthesized. The dispersed microstructure of the clays in the nanocomposites was characterized by small angle neutron scattering (SANS), ultra small angle neutron scattering (USANS), small angle X-ray scattering (SAXS), and high-resolution transmission electron microscopy (HR-TEM).<sup>18</sup> All clays were highly delaminated and well dispersed within their host matrices. The mean number of individual clay platelets per tactoid was predicted by fitting SANS data to the stacked-disk model and measured directly from HR-TEM images of a large number of tactoids in each sample. SANS results were in good agreement with HR-TEM for composites with low clay concentrations (0.5 wt%), however deviations were observed at higher clay loadings (2.0wt%). These deviations are discussed in terms of several factors not taken into account by the stacked-disk model: (a) long-range interactions, which become more important at high loadings; (b) departure of tactoid geometries from parallel stacks of rigid disks; (c) the polydispersity of tactoid thicknesses.<sup>18</sup>

SAXS peaks were not present for most of the synthesized nanocomposites suggesting a high degree of clay delamination was achieved.<sup>18</sup> However, a broad peak was observed for the 2.0wt% I-44pa clay nanocomposite, indicating the presence of some larger tactoids than in the other nanocomposites having a range of d-spacings. The HR-TEM measured distributions of clay platelet *d*-spacings in tactoids dispersed within the nanocomposites which were in the range from 8-20Å (12-15 Å average), indicating that the quaternary ammonium ion pillarating agents were no longer present. These quaternary salts either decomposed during the high-temperature (260°C) stage of curing or were not

fully exchanged with the interlayer cations present between all platelet interlayers during the original clay modification. Clay/polyDCPD composites were also prepared using PGW clay modified by poly(ethyleneglycol).<sup>18</sup> This clay dispersed more rapidly, needing less sonication than the other clays. The resistance to delamination of all nanocomposites studied increased with greater clay loading under equivalent synthesis conditions.

A method of visualization of the nanophlatelets present in clay nanocomposites was developed.<sup>19</sup> The exfoliation and dispersion of nanoclays particles (0.5 & 2% by weight) in a polymer matrix is analyzed using the Scanning Electron Microscope (SEM) and TEM, after a low temperature air plasma etch. The plasma etch preferentially removes the polymer to expose the nanoparticles. SEM analysis illustrate the results of the etching in the top and 45° surfaces of nanoclays filled polymer. The I-28 clay was dispersed in monomeric dicyclopentadiene (DCPD) using sonication (3h) and high shear mixing, followed by curing via ring-opening polymerization catalyzed by a Grubbs-type ruthenium catalyst.

Highly delaminated clay in the liquid monomer, dicyclopentadiene, were oriented under shear and then a portion of that orientation was captured by in-situ polymerization.<sup>20</sup> Highly delaminated dispersions of the organically modified day I-28 (Nanocor, Inc.) in liquid dicydopentadiene (DCPD) were prepared. In-situ ring-opening metathesis polymerization of I-28/DCPD nanodispersions generated I-28/poly(dicydopentadiene) nanocomposites. When day/DCPD dispersions were cured under sheer, alignment of day platelets, tactoid and small particulates were captured. This orientation were confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The Herman's orientation parameter were calculated for the oriented composites.<sup>20</sup> Viscosities of the liquid nanodispersions exhibited thixotropic flow behavior, prior to curing. The time-dependent viscosity effects became more pronounced with an increase in delamination. Initial viscosities increased with progressive day platelet generation during delamination and nanodispersion within the liquid monomer. Viscosity can be used to follow day exfoliation/delamination.<sup>20</sup> Treating the surface of a 2 wt% I-28 day/poly(DCPD) nanocomposite with oxygen plasma eroded the matrix, exposing day tactoids protruding from the surface. These surfaces were examined by SEM and energy dispersive X-ray spectroscopy (EDS).

#### Vapor-Grown Carbon Nanofiber Composites.<sup>21-23</sup>

The ablation, mechanical and thermal properties of vapor grown carbon fiber (VGCF) (Pyrograff III™ Applied Sciences, Inc.)/phenolic resin (SC-1008, Borden Chemical, Inc.) composites were evaluated to determine the potential of using this material in solid rocket motor nozzles.<sup>21</sup> Composite specimens with varying VGCF loadings (30-50% wt.) including one sample with ex-rayon carbon fiber plies were prepared and exposed to a plasma torch for 20 s with a heat flux of 16.5 MW/m<sup>2</sup> at approximately 1650 °C. Low erosion rates and little char formation were observed, confirming that these materials were promising for rocket motor nozzle materials. When fiber loadings increased, mechanical properties and ablative properties improved.

The VGCF composites had low thermal conductivities (approximately 0.56 W/m-K) indicating they were good insulating materials.<sup>21</sup> If a 65% fiber loading in VGCF composite could be achieved, then ablative properties are projected to be comparable to,

or better than, the composite material currently used on the Space Shuttle Reusable Solid Rocket Motor (RSRM).

Since vapor-grown carbon fibers are good conductors with high aspect ratios, the conductivities of a series of these fibers in crosslinked polymers were investigated.<sup>22</sup> Since these fibers are highly nested and entangled, separating and completely dispersing the nests as random individual fibers is a major problem that must be overcome to obtain better composite properties.

Vapor grown carbon nanofiber (VGCF/vinyl ester composites were prepared.<sup>22</sup> Their volume electrical properties exhibited percolation behavior with a sharp drop in resistivity occurring between 2 and 3 wt% VGCF loading. Composites made from nitric acid-oxidized VGCF were insulators even at: 15 wt% VGCF loading. Unpolished samples had thin resin-rich outer layers observed by SEM, which affected their resistivity behavior. The effects of fiber diameter, heat treatment and fiber/resin mixing were examined. Incorporating VGCF had little influence on flexural moduli, decreased flexural strengths and  $T_g$  and increased storage moduli,  $E'$ , both above and below  $T_g$ .

**Gas sensitive vapor grown carbon nanofiber/polystyrene sensors.**<sup>23</sup> A new class of conductive composites with good gas sensitivity was fabricated by filling polystyrene with vapor grown carbon nanofibers (VGCFN).<sup>23</sup> A solution mixing/solvent removal procedure was used.<sup>23</sup> VGCFNs form conductive networks at fiber loadings above the percolation limit within the matrix. Greatly improved conductivity is achieved relative to the same volume fraction of carbon black addition when these fibers are distributed to give reasonably uniform dispersions in the matrix. The high aspect ratios of these fibers (~70 to 250 nm diameters and 5 ~75  $\mu\text{m}$  lengths) assist in forming low wt% percolation thresholds (below 1 wt% fiber).

Excellent gas sensitivity was achieved upon exposure, exhibited by an increase in resistance by  $10^4$ - $10^5$  times higher than the original resistance value in many saturated organic vapors.<sup>23</sup> A maximum resistance response of about  $1.1 \times 10^5$  times exposure to saturated THF vapor at 6.25 wt% of VGCFN in the polystyrene matrix was observed.<sup>23</sup> The maximum resistance response declined from about  $2.0 \times 10^5$  times at 15 °C to about  $3.4 \times 10^4$  times at 55 °C.<sup>23</sup> These composites exhibited stable and reusable gas sensitivity to THF vapor.<sup>23</sup> Carbon black/polystyrene composites exhibit a negative vapor coefficient (NVC) upon swelling caused by filler redistribution. In contrast, VGCFN/polystyrene composites are more stable, with much smaller NVC values due to their high aspect ratios and reinforcing effects which stabilize electrical percolation pathways. Thus, VGCFN/organic polymer composites are good gas sensor candidates for detecting organic vapors.<sup>23</sup>

**Electromagnetic shielding properties of carbon fiber composites.** EMI shielding is important for electronic equipment functioning and for security reasons. Vapor grown carbon nanofibers were mixed with monomers or resins to make shapeable pastes and puttied which can be molded or caulked into openings before curing.<sup>24</sup> Thus, they could be widely applicable for EMI shielding applications. Composite materials incorporating VGCF may produce greater homogeneity and isotropy with regard to the electrical properties of the material. The production of VGCF/VE composites with uniform electrical properties may yield cost efficient, corrosion resistant, durable composites with significant electromagnetic shielding effectiveness. Critical factors in

the shielding performance of the VGCF/VE composite include the fiber length, fiber diameter, fiber conductivity and distribution of the fibers within the material.

Shielding effectiveness measurements have been performed on a vapor grown carbon fiber (VGCF)/vinyl ester (VE) composite material over a frequency range of 10 MHz to 1 GHz using a dual TEM (DTEM) cell along with a vector network analyzer.<sup>24</sup> A VGCF/VE composite sample containing 15% carbon fiber by weight was utilized in the measurements. The electric and magnetic shielding effectiveness of the VGCF/VE composite were measured in the form of electric and magnetic field insertion losses. The shielding effectiveness results for the VGCF/VE composite were shown to exhibit significant variation with regard to the placement of the composite sample in the DTEM cell.<sup>24</sup> The electric field insertion loss of the VGCF/VE composite was more highly variable from measurement to measurement than the magnetic field insertion loss.

**Nitric acid surface oxidations of vapor grown carbon nanofibers.<sup>25</sup>**

Vapor grown carbon nanofibers (Pyrograf III) with 100–300 nm diameters and ~10–100 lm lengths were oxidized in 69–71 wt.% nitric acid (115 °C) for various times (10 min to 24 h).<sup>25</sup> These fibers were remarkably oxidation-resistant. XPS (O<sub>1s</sub>) showed that the surface atomic oxygen percent increased from 6.3 to 18.3–22.5% for 10–90 min. oxidations followed by a drop to 14–15% after 10–24 h oxidations.<sup>25</sup> No damage was observed by TEM. Little change in surface area was observed by N<sub>2</sub> BET, but CO<sub>2</sub>-DR measurements exhibited an increase from 20–25 m<sup>2</sup>/g to 41–73 m<sup>2</sup>/g after 10–90 min. of oxidation followed by a decrease to 35–22 14 m<sup>2</sup>/g after 10 h, consistent with the XPS findings. Shallow ultramicropore formation could account for the surface area increase. NaOH titrations showed ~3-fold increase in surface acidic functions (~27 to 76 μmol/g) occurring after 10 min. of oxidation. Then this level remained constant through 24 h of oxidation. XPS (C<sub>1s</sub>, O<sub>1s</sub>) confirmed that carboxyl groups were removed and ester, anhydride, quinoid and phenolic hydroxyls appeared upon HNO<sub>3</sub> oxidation.<sup>25</sup> Oxidized fibers dispersed when shaken in water, demonstrating wettability had increased. A model for this oxidation behavior is proposed.<sup>25</sup>

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